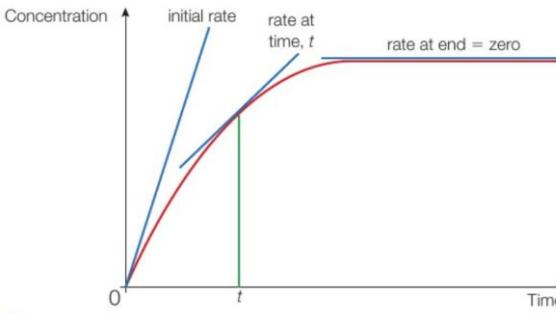
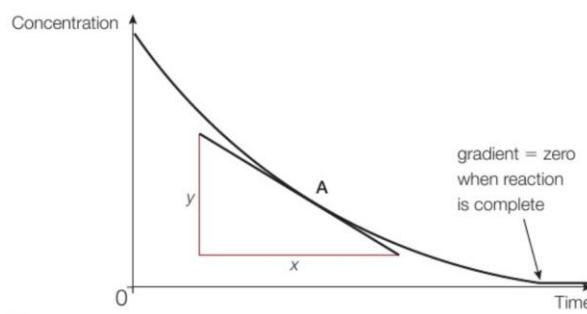


Topic 9: Introduction to Kinetics and Equilibria

9A: Kinetics

Students will be assessed on their ability to:

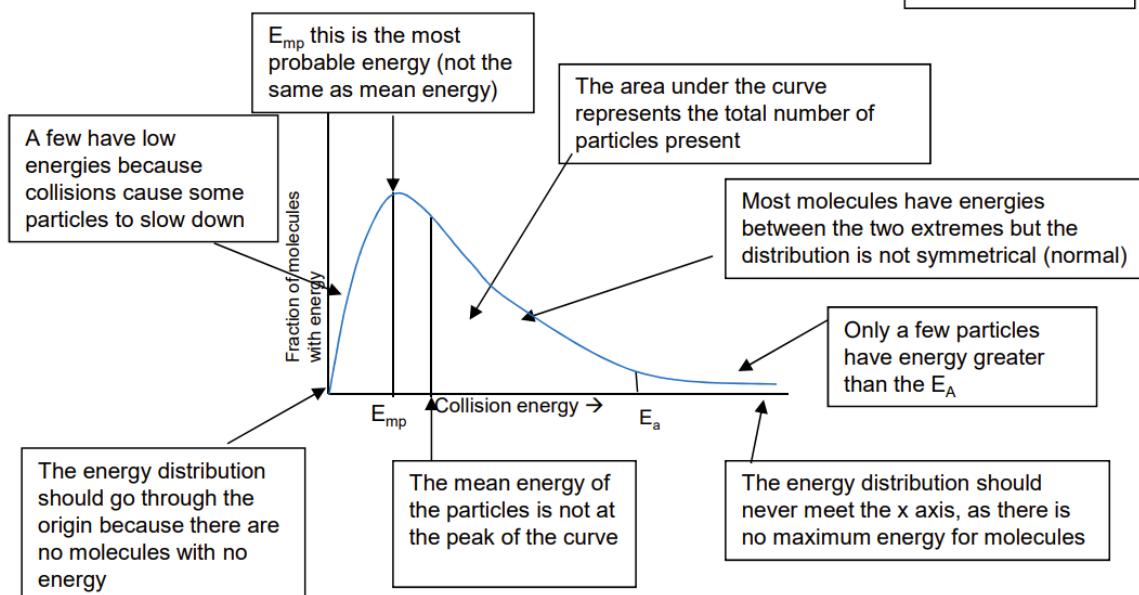
9.1	<p>understand, in terms of the collision theory, the effect of changes in concentration, temperature, pressure and surface area on the rate of a chemical reaction</p>
	<p>The rate of reaction is "the change in concentration of a substance in unit time"</p> <p>Effect of Concentration</p> <p>For reactions in solutions, an increase in concentration often causes an increase in reaction rate as there are more particles per unit volume which results in an increase in frequency of successful collisions between particles</p> <p>There are more successful collisions per second and so rate of reaction often increases</p> <p>Effect of Pressure</p> <p>For reactions in the gas phase, an increase in pressure will cause an increase in the rate of reaction as there are more reactant molecules per unit volume of mixture which results in an increase in frequency of successful collisions</p> <p>Effect of Surface Area</p> <p>For heterogeneous reactions involving a solid, a larger surface area of the solid will result in an increase in frequency of successful collisions between reactant particles and so results in a faster reaction</p> <p>Effect of Temperature</p> <p>An increase in temperature increases the average kinetic energy of molecules so more collisions have energy greater than or equal to the activation energy</p>
9.2	<p>understand that reactions take place only when collisions have sufficient energy, known as the activation energy</p>
	<p>Reactions can only occur when two molecules collide with each other with sufficient minimum energy and in the correct orientation</p> <p>The energy is usually needed to break the relevant bonds in one or either of the reactant molecules</p> <p>This minimum energy that colliding particles must possess for a reaction to occur is called the Activation Energy, E_a</p>
9.3	<p>be able to calculate the rate of a reaction from:</p> <ul style="list-style-type: none"> i the time taken for a reaction, using $\text{rate} = 1/\text{time}$ ii the gradient of suitable graph, by drawing a tangent, either for initial rate, or at a time, t
	 <p>fig B A graph showing the concentration of a product against time.</p>  <p>fig A A graph showing the concentration of a reactant against time.</p> <p>Initial rate is the rate at the start of the reaction where it is fastest</p> <p>When a graph of concentration of reactant (or product) is plotted against time, the gradient (or slope) of the graph indicates the initial rate of reaction or at a time, t (unit is in $\text{mol dm}^{-3} \text{s}^{-1}$)</p>

9.4

understand qualitatively, in terms of the Maxwell-Boltzmann distribution of molecular energies, how changes in temperature affect the rate of a reaction

The Maxwell-Boltzmann energy distribution shows the spread of energies that molecules of a gas or liquid have at a particular temperature

Learn this curve carefully



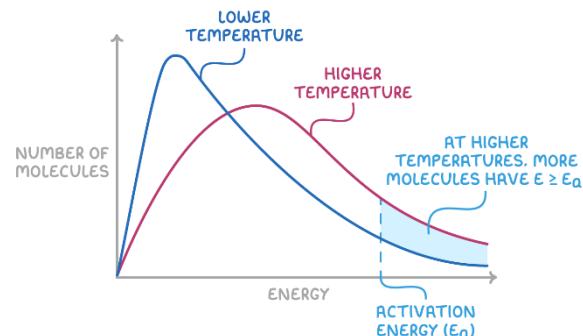
Q. How can a reaction go to completion if few particles have energy greater than E_a ?

A. Particles can gain energy through collisions

Effect of Temperature in terms of Maxwell-Boltzman Distribution

An increase in temperature increases the fraction of molecules that possess the required activation energy. The rate of the reaction increases because the number of successful collisions per second increases

Area under curve to the right of the activation energy line represents the fraction of molecules that has enough energy for the collisions to be successful



9.5

understand the role of catalysts in providing alternative reaction routes of lower activation energy

A **catalyst** is a substance that increases the rate of a reaction without being chemically changed or used up in the reaction

Catalysts provide an alternative reaction pathway that requires a lower activation energy so more collisions have energy greater than the activation energy

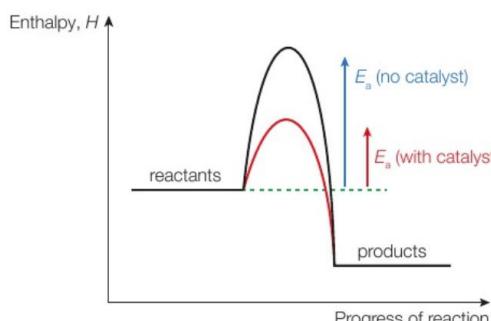


fig C Simplified reaction profiles for an uncatalysed and a catalysed reaction.

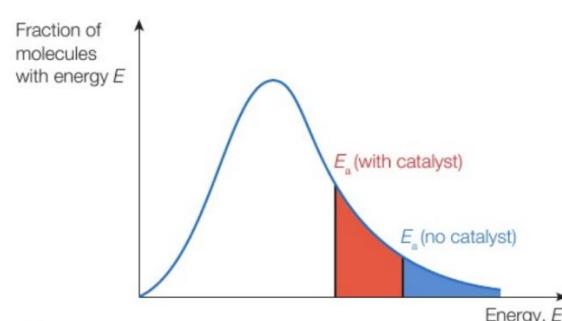
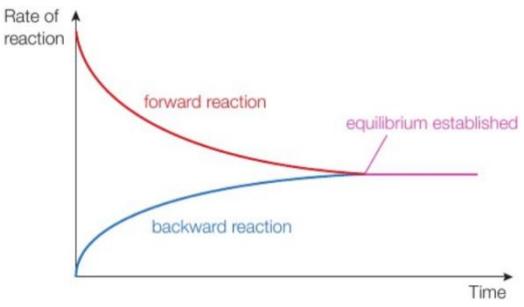


fig A A graph showing the effect on the fraction of molecules that have the required energy to react when a catalyst is present.

9.6	be able to draw the reaction profiles for uncatalysed and catalysed reactions, including the energy level of the intermediate formed with the catalyst
	<p>▲ fig D Enthalpy profile diagram for a catalysed reaction involving the formation of an intermediate.</p>
9.7	understand the use of catalysts in industry to make processes more sustainable by using less energy and/or higher atom economy
	Economic Advantages of using Catalysts: <ul style="list-style-type: none"> More desired product can be obtained per unit time as catalysts increase the rate of reaction with little or no by-products Reactions can take place at lower temperatures which results in lower energy costs Catalysts allow fewer steps in the overall reaction so results in less energy costs Percentage yield for each step may be higher (with fewer steps) Less product loss in separation
9.8	be able to interpret the action of a catalyst in terms of a qualitative understanding of the Maxwell-Boltzmann distribution of molecular energies
	<p>Further suggested practical</p> <p>Experiments to demonstrate the factors that influence the rate of chemical reactions, including the decomposition of hydrogen peroxide, reaction of marble chips with acid, reaction of thiosulfate ions with acid</p>

9B: Equilibria

Students will be assessed on their ability to:

9.9	<p>know that many reactions are readily reversible and that they can reach a state of dynamic equilibrium in which:</p> <ul style="list-style-type: none"> i the rate of the forward reaction is equal to the rate of the backward reaction ii the concentrations of the reactants and the products remain constant 																											
	<p>Two conditions for dynamic equilibrium to be established:</p> <ol style="list-style-type: none"> 1. Reaction must be reversible 2. Reaction mixture must be in a closed container <p>Three features that define a system that is in dynamic equilibrium:</p> <ol style="list-style-type: none"> 1. The rate of forward reaction is equal to the rate of backward reaction 2. The concentrations of the reactants and products remain constant 3. Both forward and backward reactions are continuously occurring 																											
9.10	<p>be able to predict and justify the qualitative effects of changes of temperature, pressure and concentration on the position of equilibrium in a homogeneous system</p>																											
	<p>Effect of changes in Concentration</p> <p>If we increase the concentration of one of the reactants in a system in equilibrium, the rate of forward reaction will increase and more products will form. As the concentration of products increases, the rate of backward reaction will also increase and eventually a new equilibrium is established to the right than the original</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr style="background-color: #e0f2e0;"> <th style="padding: 2px;">Concentration (reactants)</th> <th style="padding: 2px;">Concentration (products)</th> <th style="padding: 2px;">Position of Equilibrium shift</th> </tr> </thead> <tbody> <tr> <td style="padding: 2px;">Increased</td> <td style="padding: 2px;"></td> <td style="padding: 2px;">To the right</td> </tr> <tr> <td style="padding: 2px;">decreased</td> <td style="padding: 2px;"></td> <td style="padding: 2px;">To the left</td> </tr> <tr> <td style="padding: 2px;"></td> <td style="padding: 2px;">Increased</td> <td style="padding: 2px;">To the left</td> </tr> <tr> <td style="padding: 2px;"></td> <td style="padding: 2px;">decreased</td> <td style="padding: 2px;">To the right</td> </tr> </tbody> </table> <p>Effect of changes in Pressure</p> <p>At a given temperature, the pressure of a gaseous mixture depends only on the number of gas molecules in a given volume</p> <p>The effect of changes in pressure depends on the total number of moles on each side of the balanced equation</p> <p>This table shows what happens when pressure is increased:</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr style="background-color: #e0f2e0;"> <th style="padding: 2px;">No. of moles of reactants</th> <th style="padding: 2px;">No. of moles of products</th> <th style="padding: 2px;">Position of Equilibrium shift</th> </tr> </thead> <tbody> <tr> <td style="padding: 2px;">More</td> <td style="padding: 2px;">Fewer</td> <td style="padding: 2px;">To the right</td> </tr> <tr> <td style="padding: 2px;">Fewer</td> <td style="padding: 2px;">More</td> <td style="padding: 2px;">To the left</td> </tr> <tr> <td style="padding: 2px;">Same</td> <td style="padding: 2px;">Same</td> <td style="padding: 2px;">No change</td> </tr> </tbody> </table> <p>The reverse changes are true for a decrease in pressure</p> <p>Effect of changes in Temperature</p> <p>If we increase the temperature, both the rate of forward and backward reactions will increase but the increase in the rate of the endothermic reaction will be greater than the increase in the rate of the exothermic reaction</p> <div style="border: 1px solid black; padding: 5px; margin-top: 10px;"> <p>Typical Exam question: What effect would increasing temperature have on the yield of ammonia?</p> $N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = -ve \text{ exo}$ <p>Exam level answer : must include bold points</p> <p>If temperature is increased the equilibrium will shift to oppose this and move in the endothermic, backwards direction to try to decrease temperature. The position of equilibrium will shift towards the left, giving a lower yield of ammonia.</p> </div>	Concentration (reactants)	Concentration (products)	Position of Equilibrium shift	Increased		To the right	decreased		To the left		Increased	To the left		decreased	To the right	No. of moles of reactants	No. of moles of products	Position of Equilibrium shift	More	Fewer	To the right	Fewer	More	To the left	Same	Same	No change
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	<p>An increase in temperature will shift the position of equilibrium in the direction of the endothermic reaction</p> <table border="1"> <thead> <tr> <th>Temperature change</th><th>Thermicity of forward reaction</th><th>Position of Equilibrium shift</th></tr> </thead> <tbody> <tr> <td>Increased</td><td>Exothermic ($\Delta H -$)</td><td>To the left</td></tr> <tr> <td>Decreased</td><td>Exothermic ($\Delta H -$)</td><td>To the right</td></tr> <tr> <td>Increased</td><td>Endothermic ($\Delta H +$)</td><td>To the right</td></tr> <tr> <td>Decreased</td><td>Endothermic ($\Delta H +$)</td><td>To the left</td></tr> </tbody> </table> <p>Effect of adding a Catalyst</p> <p>If a catalyst is added, both the rate of forward and backward reaction will increase by the same amount so position of equilibrium is not altered, but will speed up the rate at which equilibrium is reached</p>	Temperature change	Thermicity of forward reaction	Position of Equilibrium shift	Increased	Exothermic ($\Delta H -$)	To the left	Decreased	Exothermic ($\Delta H -$)	To the right	Increased	Endothermic ($\Delta H +$)	To the right	Decreased	Endothermic ($\Delta H +$)	To the left
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9.11	evaluate data to explain the necessity, for many industrial processes, to reach a compromise between the yield and the rate of reaction															
	<p>The Haber Process</p> <p>$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = -$ (exothermic)</p> <p>Low temperatures give good yield and is ideal for the iron catalyst to work effectively but rate of reaction will be slow and maintaining high temperature is uneconomical due to high energy costs so a compromise temperature of 450C is used</p> <p>High pressure gives good yield and fast rate of reaction as well but high energy costs to produce and maintain this pressure so a compromise pressure of 250atm is used</p> <p>The Contact Process</p> <p>Stage 1: $S(l) + O_2(g) \rightarrow SO_2(g)$</p> <p>Stage 2: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -96 \text{ kJ/mol}$</p> <p>As forward reaction is exothermic, low temperature favours high yields of SO_3 but rate of reaction will be slow as catalyst won't work effectively at low temperatures so a compromise temperature of 450C is used</p> <p>High pressure would increase the yield as there are fewer moles of gas on the right hand side of the balanced equation but too high a pressure will result in high energy costs so a compromise pressure of 2atm is used</p> <p>A catalyst of vanadium(V)oxide is used</p> <div style="border: 1px solid black; padding: 5px;"> <p>In all cases catalysts speeds up the rate allowing lower temp to be used (and hence lower energy costs) but have no effect on equilibrium</p> </div> <div style="border: 1px solid black; padding: 5px;"> <p>In all cases high pressure leads to too high energy costs for pumps to produce the pressure and too high equipment costs to have equipment that can withstand high pressures.</p> </div> <p>Recycling unreacted reactants back into the reactor can improve the overall yields of all these processes</p>															
	<p>Further suggested practicals:</p> <p>Demonstrate the effect of a change of temperature, pressure and concentration on a system at equilibrium:</p> <ul style="list-style-type: none"> i chlorine reacting with iodine to form iodine(I) chloride, which then reacts with chlorine to form iodine(III) chloride ii the equilibrium system between nitrogen dioxide (NO_2) and dinitrogen tetroxide (N_2O_4) 															